STATE OF CALIFORNIA

AIR RESOURCES BOARD

AIR MONITORING QUALITY ASSURANCE

VOLUME V

AUDIT PROCEDURES
FOR
AIR QUALITY MONITORING

APPENDIX J

PERFORMANCE AUDIT PROCEDURES
FOR
THROUGH-THE-PROBE-TOXIC AUDITS

MONITORING AND LABORATORY DIVISION

AUGUST 2002

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STATE OF CALIFORNIA

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APPENDIX J.1

PERFORMANCE AUDIT PROCEDURES
FOR
THROUGH-THE-PROBE-TOXIC AUDITS

MONITORING AND LABORATORY DIVISION

AUGUST 2002

J.1.0 INTRODUCTION

J.1.0.1 GENERAL INFORMATION

Toxic through-the-probe audits are conducted annually at each site by the Quality Assurance Section (QAS). A sample canister is filled with known (assigned) concentrations of audit gases during a twenty-four hour period. The sampler is run, whenever possible, in conditions duplicating a routine ambient run. The analytical laboratory is not notified of the audit until after it analyzes the sample. The QAS then requests the analytical results and calculates the percent bias of the sample for various volatile organic compounds VOC's:

$$\text{Percent Bias} = \frac{(\text{Measured Conc.* - Assigned Conc.*})}{\text{Assigned Concentration}} \text{ X } 100$$

The purpose of a through-the-probe toxic audit is to assess the accuracy of the total measurement system, including: errors inherent in contamination in transport, effects of sample pump and probe, as well as laboratory error.

J.l.0.2 FIELD NOTIFICATION

The QAS arranges the audit with the station operator ten days to two weeks before the audit date. If the station is operated by ARB, the auditor is to supply a sampling canister. Call the Organics Laboratory to obtain a sampling canister. If the site is operated by a District or other entity, the station operator is responsible for supplying the sample canister. Inform the operator to provide a canister for the audit. The station operator is requested not to inform the laboratory that the sample is an audit sample. No special or differentiating markings are put on the canister.

J.l.0.3 CAUTIONS

Avoiding contamination is critical since the organic compounds being generated by the dilution system are present in low concentrations, generally in the 0.10 to 5.0 ppb range. All stainless steel (SS) and Teflon® lines and fittings in the dilution apparatus must be cleaned periodically and capped when not in use. Further, during each audit there must be a <u>positive</u> pressure at the manifold "T"
(1 liter/per minute minimum bypass flow) where the dilution system output connects to the sample probe.

NOTE: The cleaning procedure is performed every 120 days. All Teflon® and SS lines in the dilution system are flushed with a Liqui-NO_x™** solution followed by distilled water and air dried. All SS fittings are soaked in a Liqui-NO_X ™ solution and cleaned ultrasonically. Furthermore, the Environincs 2014 is certified quarterly to ensure proper operation.

* Conc. = Concentration
** Trademark – DuPont Corporation

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PERFORMANCE AUDIT PROCEDURES
FOR
THROUGH-THE-PROBE-TOXIC AUDITS

MONITORING AND LABORATORY DIVISION

AUGUST 2002

J.2.0 AUDIT PROCEDURES

J.2.0.l APPARATUS

1. Dilution unit (Environics 2014) with humidifier rail and attachments
2. Toxic gas cylinder with SS regulator
3. Vol-o-Flow gauge (0-5 LPM)
4. 1/4” Teflon tubing with spare fittings
5. 1/8” Aculife treated stainless steel tubing with spare fittings
6. Portable API 701 clean air generator
7. Drain cup/bottle
8. “Clean” sampling canister
9. RH meter and temperature gauge
10. Nanopure water
11. Table (optional)

J.2.0.2 DETERMINATION OF DILUTION RATIO

The dilution ratio to be used for the audit is defined as follows:

$$\text{Dilution Ratio} = \frac{\text{Gas Flow}}{\text{Air Flow + Gas Flow}}$$

This ratio is calculated, approximately, prior to the audit, and depends on several factors including assigned cylinder concentrations, required minimum air flow, gas flow (cannot exceed 100 cubic centimeters per minute (CCPM)) and the requirement to generate VOC concentrations greater than the minimum detectable limit to permit quantitative lab analyses. In general, the desired concentration of VOC’s in the audit gas stream is in the range of 0.1 to 5.0 ppb. Once the desired concentration is chosen, the dilution ratio and then the required flow settings are determined according to the following example for chloroform ($CHC1_3$).

1. Desired gas concentration (assigned value): 0.2 ppb $CHC1_3$

   Assigned NIST Cylinder Value: 20.00 ppb $CHC1_3$

   $$\text{Dilution Ratio, calculated} = \frac{0.20\ \text{ppb}}{20.00\ \text{ppb}} = \frac{1}{100}$$

NOTE: Typically, the concentrations of the remaining VOC’s in the cylinder are in the same range as $CHC1_3$ so the calculated dilution ratio permits quantitative analyses of all compounds.

2. If we find the probe flow measures 2.5 LPM (Ref: Sect. J.2.0.3, Step 4) and we require a manifold bypass flow of 1.0 LPM:

   Required Air Flow = 2.5 LPM + 1.0 LPM
   = 3.5 LPM (True Flow)
   = 3500 CCPM

   Thus, 3.5 LPM of total flow is required to create 1.0 LPM of bypass.

3. Then substitute and solve for Gas Flow:

$$\text{Dilution Ratio} = \frac{\text{Gas Flow}}{\text{Air Flow + Gas Flow}}$$

$$\frac{1}{100} = \frac{\text{Gas Flow}}{3.5 + \text{Gas Flow}}$$

$$\begin{aligned}\text{Gas Flow} &= 0.0354 \text{ LPM} \\ &= 35.4 \text{ CCPM (True Flow)}\end{aligned}$$

Thus, 35.4 CCPM of gas flow is required.

4. Correct the flows by using the dilution system correction equations from the Laboratory's latest calibration report (certified every quarter), calculate the required air and gas display readings for the dilution unit. The front display and key pad will be used to set the flow rates for the desired flow. The following results are from a typical calibration where slope and intercept for the gas MFM are 0.9988 and 0.6174, respectively, and 1.0026 and 0.0828 for the air MFM, respectively.

NOTE: The display flow rate is the target flow rate and not the actual flow rate.

<u>Gas</u>: Display = 0.9988 x True Flow + 0.6174
= 0.9988 x 35.4 + 0.6174
= <u>35.97 CCPM</u>

<u>Air</u>: Display = 1.0026 x True Flow + 0.0828
= 1.0026 x 3.5 + 0.0828
= <u>3.59 LPM</u>
= <u>3590 CCPM</u>

5. Thus, the Environics air flow (port #1) will be set at 3590 CCPM and the gas flow (port #3) will be set at 36 CCPM for the audit (rounded from 35.97 CCPM).

J.2.0.3 <u>STATION PREPARATION</u>

1. Perform leak check #1 (see Section J.2.0.5.1).

2. Ensure the sample canister valve is closed after leak check #1 and disconnect the line from the canister.

3. Switch on the sampler (timer override on "I", the manual ON position). Verify that the back pressure and sample flow are correctly set (ref: Q.A. Manual, Volume II, Appendix Q).

4. Connect a Vol-o-Flow gauge (vacuum side) to the end of the probe line to determine the sampler flow demand. Record the vacuum reading on the Toxics Worksheet (Figure J.2.0.1).

5. Perform leak check #2 (see Section J.2.0.5.2).

NOTE: Both leak checks should be completed before any gas is introduced into the system via the Environics.

6. Attach a stainless steel ¼ inch "T" (see Figure J.2.0.2) to the end of the station's probe using a Teflon® or stainless steel nut and ferrule. Connect the leg that would flow "straight through" to a ¼" Teflon® line, via a stainless steel or Teflon® nut and ferrule, to serve as a bypass line. Connect the "T" portion (90 degree angle to the other two) of the stainless steel "T" to a ¼" Teflon® line and connect the other end to the output port of the Environics 2014. The bypass line will be used to measure bypass flow rates using the Vol-o-Flow.

CAUTION: When there is a possibility of overnight temperatures, shorten all outside lines (by pulling excess inside the building) to ensure that there is no coiling of the line as the humidified gases may freeze and block the line. Also ensure that the bypass line is straight enough to allow condensed water droplets to drain from the line.

NOTE: If it is not feasible to connect to the stations sample probe inlet, the connection can be made at the input port of the Xontech 910. The bypass "T" is still used but the bypass line must be vented outside of the building.

J.2.0.4 DILUTION SYSTEM PREPARATION

(Refer to Figure J.2.0.2 for a diagram of toxic audit setup.)

1. Connect the output port of the API to port #1 of the Environics. Ensure fittings are snug. Do not overtighten as the threads on the ports are easily stripped or damaged.

2. Connect a ¼" Teflon® line to the vent port of the Environics and ensure the end of the line is outside of the building. Failure to do so will allow various gases to accumulate inside of the building.

3. Install humidifier flask and tubing (See Figure J.2.0.3). Disconnect the quick disconnect on the drain line. Fill flask with nanopure water. Place the end of the drain line in a drain cup and reconnect the quick disconnect. Water will now flow through the humidifier rail and tubing. Once all air bubbles have been flushed out of the rail and tubing, disconnect the quick disconnect. Refill flask. Humidification system is now operational. Ensure that stopcock on flask remains open for the duration of the audit so water can flow into the humidifier rail.

4. It is now safe to switch on the API and Environics. NEVER switch on the API without having installed the API output port to the #1 port of the Environics. Failure to do so will cause humidification and contamination of the API and invalidate all audit results until it is certified clean.

5. Once the API has pressurized and stabilized, enter into flow mode (by pressing the soft key) on the Environics and set port #1 to the air flow you determined in your dilution ratio earlier. This is the beginning of the 1 hour air purge. Record your start time and end times when completed. Proceed to the next step while waiting.

6. With your Vol-o-Flow, measure the bypass flow at the bypass line located at the stainless steel "T" that is connected to the probe inlet. Bypass should be at least 1.0 lpm.

7. Connect a stainless steel regulator to the toxic gas audit cylinder. Purge the regulator three times by opening and closing the regulator briefly. Connect a 1/8" Aculife treated stainless steel line from the regulator to port #3 of the Environics. Pressurize the gas line by setting your regulator to 25psi. Once pressurized, shut off the regulator by turning it counter-clockwise until it stops. Note the regulator pressure. In 5 minutes, check pressure on regulator again. If it is still at the set pressure (roughly 25psi), the line is free of leaks. If the pressure has fallen, re-check line for cracks and fittings for leaks.

   CAUTION: Do not proceed with the audit until you can ensure that the gas line is free of leaks. Failure to do so can drain the cylinder over the course of the audit and contaminate the building with toxic audit gases.

8. Complete appropriate sections of the Toxics Canister Worksheet (Figure J.2.0.4).

9. When you have completed a one hour air purge, you may begin a 30 minute gas purge (Refer to Section J.2.0.2 for times). Be watchful of the regulator pressure, it may drop, and adjustments may be needed for the first few minutes. Once the Environics display reads the proper flow volumes, and the regulator is stable at 25 psi, you may proceed to record all pertinent identifying data for the site, sampler and dilution system, and the dilution system correction equations on the Toxics Worksheet.

   NOTE: Only after you have completed the above steps, including leak checks and both purges, may you begin the audit.

10. Ensure that the sampler's sample line is securely connected to the canister and that the 910 has begun sampling (the counter on the 910 will be counting). If so, open canister valve. If not, wait until the 910 is sampling.

11. Verify that the 1.0 lpm bypass at the “T” has been maintained.

12. The 24-hour audit is now started. Record this on your worksheet.

J.2.0.5 LEAK CHECKS

Check the sampler and probe and canister lines for leaks as follows:

1. Leak check #1— Checking the canister sampling line for leaks (performed in Section J.2.0.3). With the sampler off, connect the output stainless steel line from the Xontech 910 to the port on the sample canister. Ensure all fittings are tight. Briefly open the valve on the sample canister, then close snugly. Record the reading on the canister gauge. Periodically monitor the canister and the 910’s gauge’s for 30 minutes. If you see a drop in vacuum at any time during the 30 minute period, retighten lines and begin leak check #1 again. A constant vacuum must be held for 30 minutes. After 30 minutes, if no leak was discovered, record the final reading. If they are different, you must find the source of the leak before proceeding as the sample canister will not be able to be pressurized properly and may also ingest ambient air while under vacuum. If the readings are the same, leak check #1 has passed. Record this on your worksheet and return to step J.2.0.3.2. If you are unable to pass leak check #1, discontinue the audit.

2. Leak Check #2 – Checking the probe line and pump for leaks (performed in Section J.2.0.3). Note the flow on the Xontech 910. Proceed to the probe inlet and cap off the probe inlet with a nut. If the probe line does not have a fitting, install one. After capping the line, allow the readings on the 910 to stabilize (should stabilize within a few minutes). Place a Vol-o-Flow gauge on the exhaust by-pass port at the rear of the sampler while the probe inlet is capped. If there is no leak, the Vol-o-Flow gauge reading should drop to zero. The indicated sample flow at the front gauge should also drop to zero. If flow reaches zero on both gauges, leak check #2 has passed. Record this on your worksheet. If flow does not reach zero on both, loosen and retighten probe nut and check all fittings to ensure they are snug. Repeat procedure. If you are unable to obtain a zero reading on both the 910 and the Vol-o-Flow there is a leak in the system. To determine where the leak is, disconnect probe cap nut and disconnect the probe line from the inlet port of the 910 and snugly cap the port. Examine the 910’s flow. If the 910 flow does not reach zero, loosen and retighten nut. If flow reaches zero, you have a leak in the probe line. If flow does not reach zero, the leak is inside of the 910. Leak check #2 will fail regardless. Record this on your worksheet discontinue audit.

J.2.0.6 END RUN PROCEDURE

1. At the end of the 24-hour audit period, record the final data readings on the Toxics Audit Data Sheet: air and gas digital flows, sampler flow, manifold bypass flow, sampler back pressure, final canister pressure, and pertinent site information: total probe length, including QA line, probe material and diameter.

2. Close the valve on the canister, disconnect the sampler output line, and record the stop time on the data sheet. Visually check that the canister has filled (pressure in sample canister should be between 8 and 12 psi) and record the final canister pressure on the toxics data sheet.

3. Set Environincs gas flow (port #3) to zero.

4. Close the main valve on the toxic cylinder and remove the SS regulator.

5. After 5 minutes of clean air purge, disconnect the “T” from the sample probe inlet and measure and record the probe flow with a Vol-o-Flow gauge as in Section J.2.0.3.4.

6. Switch off the sampler.

7. Switch off power to the API 701 and set Environics port #1 flow to zero.

8. Switch off Environics.

9. Disassemble all audit lines and cap each to prevent contamination. Cap all Environics and API ports.

10. Re-install the sample probe, as necessary, in its original location.

11. Return all station lines, timers, etc. to their original configuration.

12. Complete toxics canister worksheet.

QA AUDIT WORKSHEET
XONTECH 910 TOXIC SAMPLER

Site Name: ______________________ Site Num. __________ Date: __________

Address: ______________________ Agency: __________

Site Tech: ______________________ Auditors: __________

Quarter: 1[ ] 2[ ] 3[ ] 4[ ] Standards Version: __________ Year: __________

Sampler Information

Make and Model: ______________________

ID# ______________________

Cal. Date ______________________

Cal. Equipment Cert. Date: ______________________

Canister Fill Rate:	ccm
By-Pass Flow Rate:	lpm
Total Flow Rate:	lpm

(Total Flow Rate = Canister Fill Rate + By-pass Flow Rate)

Audit Cylinder Information		
ID#:		
Gauge Pressure	Start	Stop

Canister Information		
ID#:		
Gauge Pressure	Start	Stop

Xontech Gauge Information		
Range	"Hg	PSI
Gauge Pressure	Initial	Final

Purge and Sample Collection Times		
	Start	Stop
Xontech Internal Start-up Purge (30 minutes)		
Zero Air Purge (2 hours)		
Audit Gas Purge (30 minutes)		
Audit Gas Collection (24 hours)		

1st Leak Check-Canister (Xontech Off)	
Canister Pressure	
Start	"Hg
Stop	"Hg

2nd Leak Check-Inlet Probe (Inlet Capped Off)			
	Pass		
	Yes	No	

Environics Information
Model:
ID#:
Cal. Date:

Environics Flows	
Port #1	ccm
Port #3	ccm

Ambient Data		
	Start	Stop
Temp.		
% RH		

COMMENTS: ______________________

Figure J.2.0.1….Toxics Worksheet

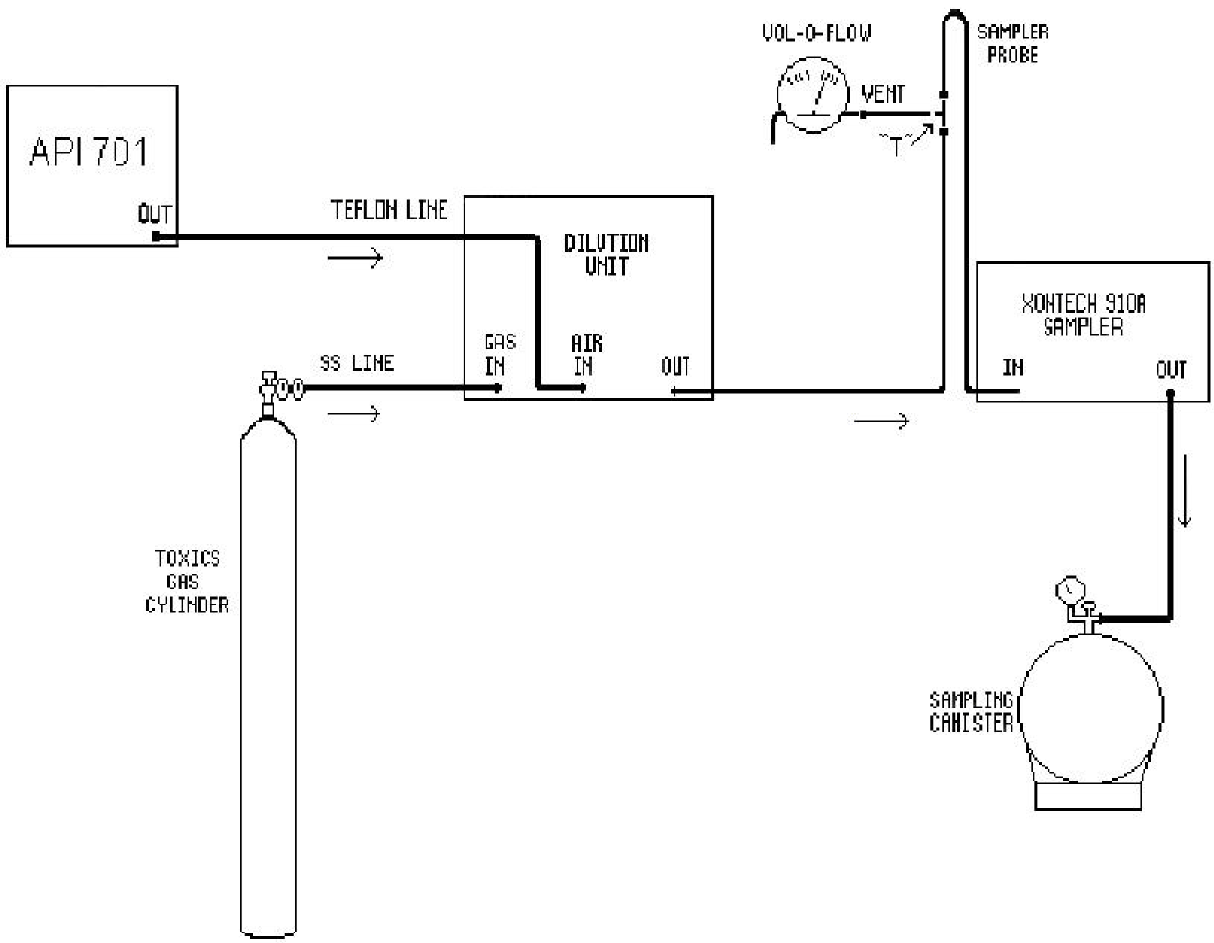

Figure J.2.0.2 ….. Toxic Audit Setup

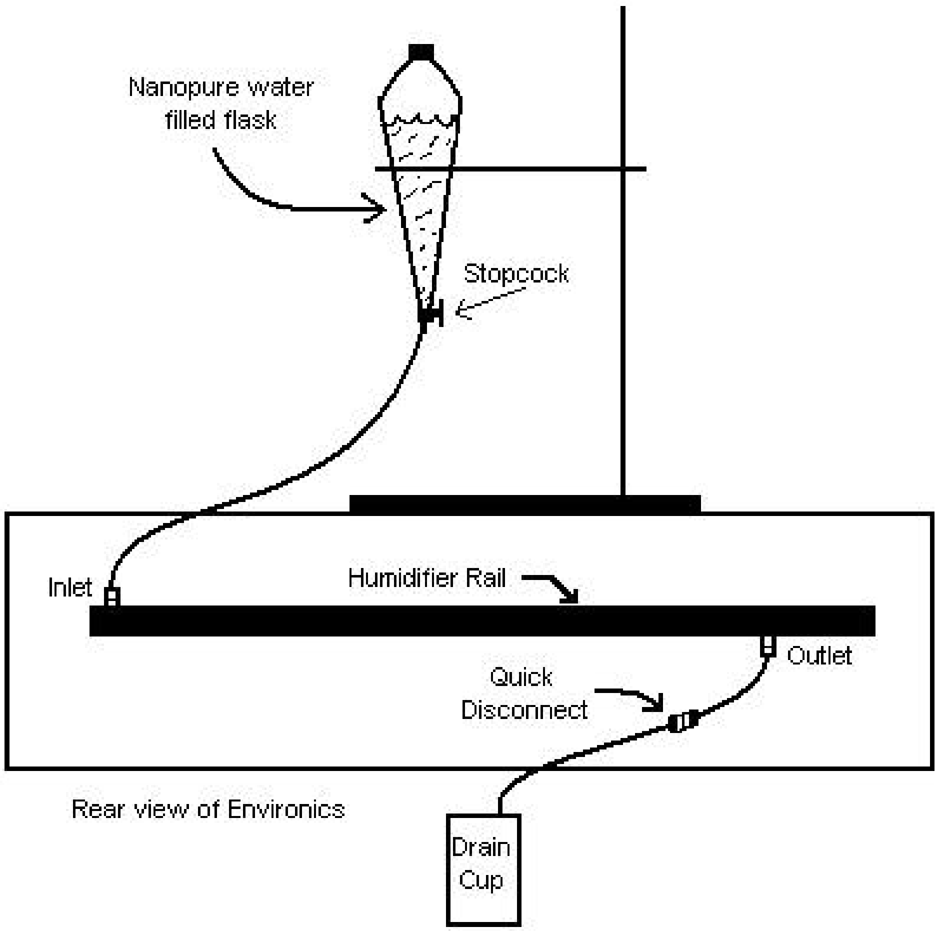

Figure J.2.0.3…..Humidifier Setup

[Place data sheet inside plastic pouch. Questions? Call Organics Lab (916) 322-2840]

CALIFORNIA AIR RESOURCES BOARD
Xontech 910A Toxics Data Sheet

Site Name: ______________________ Site Number: ______________________

Station Operator: ______________________ Sampling Date: ______________________

			CANISTER					SAMPLER			
	Date	Time (PST)	Vacuum ("Hg) LAB	Vacuum ("Hg) FIELD	Pressure (PSI) FIELD	Pressure (PSI) LAB	Pressure (PSI) LAB**	MFC Reading	Back Pressure Reading	Beginning Vacuum	Ending Pressure (PSI) FIELD
Set-Up											
Start											
Stop											

Type of Sample: [ ] Regular [ ] Collocated [ ] Trip Blank [ ] Make Up

Canister ID Number: __________ Air Sampler ID Number: __________ Date Shipped from field: ______

Sampling Conditions:
[ ] No Unusual Conditions
[ ] Wind-Blown Sand/Dust
[ ] Construction Nearby
[ ] Farm Operation Nearby
[ ] Fire Nearby
[ ] Other __________
[ ] Rain
[ ] Unknown

[ ] INVALID SAMPLE INFORMATION

Reason for Sample Invalidation:

[ ] Low canister pressure
[ ] High canister pressure
[ ] Sampling period out of range (<23 or >25 hours)
[ ] Sampling equipment inoperative
[ ] Damaged sampling media
[ ] Lab unable to provide sample media
[ ] Other reasons: ____________________

Status of Make-up Sample:

[ ] Will run make-up on: ______________

[ ] Lab unable to provide sample media
[ ] Unable to run make-up, equipment needs repair/replacement/calibration, notified Supervisor

Field Comments: ____

====FOR LABORATORY USE ONLY====

** Calibrated Gauge Pressure

Shipped to Field by: ________ Date: ________ Time: ________

Received in Lab by: ________ Date: ________ Time: ________

Bar Code:
LIMS Sample ID:

Lab Comments: ____

Bo "DataSheet Don" Lau 8/31/99

Figure J.2.0.4….Toxics Canister Worksheet

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PERFORMANCE AUDIT PROCEDURES
FOR
THROUGH-THE-PROBE-TOXIC AUDITS

MONITORING AND LABORATORY DIVISION

AUGUST 2002

J.3.0 POST AUDIT CALCULATIONS

J.3.0.1 CALCULATION OF PERCENT BIAS

After the analytical laboratory analyzes the contents of the sampling canister, obtain the lab results (measured concentrations). Calculate the percent difference for each compound in the audit sample using the following equations:

Assigned Value = Dilution Ratio x Assigned Cylinder Value.

$$\text{Percent Difference} = \frac{\text{Measured Conc. - Assigned Cylinder Value}}{\text{Assigned Cylinder Value}} \times 100$$

These calculations have been pre-programmed on the desktop computer. Sample results are shown in Figure J.3.0.1.

Quality Assurance Thru-the-Probe Toxic VOC Audit Technical Appendix

Instrument/AIRS Information

ARB Number 33144 AIRS Number 060658001 Method MLD 58

Audit Date 02/28/2001 Laboratory MLD-ORGANICS SECTION

Audit Concentration Calculations

Diluted Conc. (ppbC) = NIST Conc. * Dilution Ratio

Percent Difference = (Average - Diluted Conc.)*100/Diluted Conc.

Audit Concentation versus Laboratory Response Data

Compound	NIST Conc. (ppbC)	Dilution Ratio	Diluted Conc. (ppbC)	Run 1 (ppbC)	Run 2 (ppbC)	Run 3 (ppbC)	Average (ppbC)	Percent Difference
Dichloromethane	723.00	1/101	7.16	7.64			7.64	*6.7%*
Chloroform	22.60	1/101	0.22	0.20			0.20	*-9.1%*
1,1,1 Trichloroethane	76.80	1/101	0.76	0.72			0.72	*-5.3%*
Carbon Tetrachloride	16.50	1/101	0.16	0.15			0.15	*-6.3%*
Benzene	263.0	1/101	2.60	2.44			2.44	*-6.2%*
Trichloroethylene	95.40	1/101	0.94	0.85			0.85	*-9.6%*
Toluene	531.0	1/101	5.26	4.84			4.84	*-8.0%*
Tetrachloroethylene	76.40	1/101	0.76	0.68			0.68	*-10.5%*
Chlorobenzene	88.30	1/101						
Ethylbenzene	382.0	1/101	3.78	2.37			2.37	*-37.3%*
ortho-Xylene	84.20	1/101	0.83	0.74			0.74	*-10.8%*
m/p-Xylene	697.0	1/101	6.90	8.88			8.88	*28.7%*
Styrene	72.00	1/101	0.71	0.57			0.57	*-19.7%*
m-Dichlorobenzene	126.40	1/101	1.25	0.86			0.86	*-31.2%*
o-Dichlorobenzene	107.90	1/101	1.07	0.61			0.61	*-43.0%*
1,2 Dibromoethane	27.80	1/101						
tert-Butyl methyl ether	298.00	1/101	2.95	2.64			2.64	*-10.5%*
1,3-Butadiene	67.40	1/101	0.67	0.51			0.51	*-23.9%*

*** tert-Butyl methyl ether (MTBE) analyzed using method 50.**
*** This report is for the colocated sampler.**

California Air Resources Board
Monitoring and Laboratory Division
Quality Assurance Section

Figure J.3.0.1…Toxic Audit Report